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(NASA-CR-121007) FUEL CELL ION-EXCHANGE
MEMBRANE INVESTIGATION Final Technical
Report, 1 Mar. - 31 Aug. 1972 (Stanford
Research Inst.) 22 p HC \$3.25 CSCL 10A

N73-27928

Unclas
G3/03 10223
October 31, 1972
NASA-CR-121007

FINAL TECHNICAL REPORT

Covering period of March 1 to August 31, 1972

FUEL CELL ION-EXCHANGE MEMBRANE INVESTIGATION

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Contract NAS3-15577
SRI Project No. 1771



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FOREWORD

This final technical report represents the results obtained during the past six months in a Fuel Cell Ion-Exchange Membrane Investigation carried out at Stanford Research Institute for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, under Contract NAS3-15577.

The contract was administered by the Energy Conversion and Physical Chemistry Division of the NASA Lewis Research Center, Cleveland, Ohio. Mr. Hoyt McBryar of the NASA-Manned Spacecraft Center, Houston, Texas acted as special consultant.

This report covers work conducted from March 1 to August 31, 1972 and was prepared by Dr. M. S. Toy. Mr. J. C. DiBari assisted in the laboratory work, and the scanning electron micrographs were prepared by Dr. J. Terry.

ABSTRACT

The goal of this program is to understand the present deficiencies in the duPont fluorocarbon sulfonic acid membrane used as the solid polymer electrolyte in the General Electric H₂/O₂ fuel cell.

The work is divided into four parts: adhesives selection, elastomeric formulations, scavenger exploration, and membrane characterization.

The significant data are interpreted and recommendations are given for both short and long range further investigations in two of the four major areas: membrane adhesives and membrane stabilization.

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I INTRODUCTION

The objective of this program is to understand the deficiencies in the duPont fluorocarbon sulfonic acid membrane which is used in General Electric H₂/O₂ fuel cells.

The fixed-charge fluorocarbon sulfonic acid membrane for the H₂/O₂ fuel cell is viewed as containing fairly uniformly dispersed hydrophilic sulfonic acid (-SO₃H) groups covalently bonded to a hydrophobic polymeric fluorocarbon chain. Wet and dry cycling during fuel cell operation at General Electric suggests physical stresses in addition to chemical degradation occur resulting in membrane delamination.

A second problem associated with the fuel cell is a performance loss in the first few hours of operation. Preliminary investigations at NASA-MSC indicate the cause to be a constituent or decomposition product of the 3M AF-42 epoxy-nylon adhesive used in bonding the fuel cell elements to the polysulfone frames.

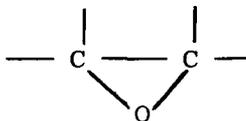
This work is divided into four parts: adhesives selection, elastomeric formulations, scavenger exploration and membrane characterization. The first three parts investigated certain concepts for correction of present deficiencies and suggested some directions and guidelines for future investigations in adhesive and membrane areas. The last part on characterization investigated the membrane involved.

II RESULTS AND DISCUSSION

Adhesives Selection

The epoxy resin adhesives have high strength, ease of application,^{1,2} relatively low surface tension, and the low viscosity of the mixes, all of which improve wetting, spreading, and penetrating action. Further advantages are the relatively long cure cycle, curing without releasing by-products (moderate term), insensitivity to moisture, and resistance to solvents. Although the epoxy resins have relatively low surface tension, untreated polyethylene and fluorocarbons are not bonded effectively by them. However, the addition of a fluorocarbon surfactant has been reported to lower the surface tension of the epoxy resin to improve wettability.¹ Modification of the properties of epoxy adhesives is commonly practiced by blending the epoxy with additives or other resins.³

In the presence of either basic or acidic materials, the highly reactive epoxide groups



readily polymerize and crosslink to form an insoluble and infusible network when the epoxide is multifunctional.

Six commercial epoxy resins were evaluated for formulation and curing studies with carboxyl perfluoroelastomers. The commercial epoxy resins are Ciba Araldite 502, 508, and 6010; ERE 1359; ECN 1280; and Dow DEN 438. The preliminary screening results shown in Table 1 were based on use of 1:1 ratio by weight of the ingredients and curing at 50°C for 4 hours.

Table 1

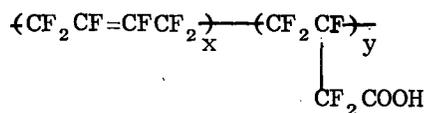
RESULTS ON SCREENING COMMERCIAL EPOXY RESINS FOR CURING
CARBOXYL PERFLUOROELASTOMERS

Epoxy Resin "FC" (COOH) _x	Ciba Araldite 508	Ciba Araldite 502	Ciba Araldite 6010	Ciba ERE 1359	Ciba ECN 1280	DOW DEN 438
Perfluoroglutaric acid	Fair	Poor	Poor	Poor	Poor	Poor
Carboxyl PPFB(I)	Fair	Weak	Good	Fair	Fair	Good
Carboxyl PPFB(II)	Fair	Poor	Fair	Fair	Poor	Good
Carboxyl Nitroso Rubber (CNR)	Poor	Poor	Poor	Poor	Fair	Good

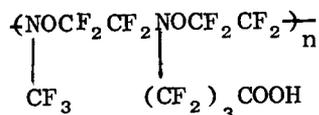
Curing temperature at 50°C for 4 hr.

For the epoxy-carboxyl perfluoroelastomer system, the reaction between the carboxyl elastomer and an epoxy resin is essentially the reaction of carboxyl groups with epoxy groups and, therefore, parallels that of the acid-cured epoxy resins or the production of epoxy ester resin vehicles.

Perfluoroglutaric acid obtained from Peninsular ChemResearch was used as a standard to compare to perfluorinated carboxyl elastomers. The chemical structure for SRI's carboxyl polyperfluorobutadiene (carboxyl PPFB) is:



where x to y ratio is about 3 or 4 to 1. The structure for Thiokol's carboxyl nitroso rubber (CNR) is:



In Table 1 carboxyl PPFB (I) is a soft near-liquid gum, which consists of a blend of polymers of molecular weights ranging from 2000 to 8000, while carboxyl PPFB (II) is more rubbery and has a narrow molecular weight of 7500. The CNR gum has a much higher molecular weight of approximately 600,000.

The commercial epoxy resin selected for formulation investigation with carboxyl perfluoroelastomer adhesives was DOW DEN 438.

Elastomeric Formulations

The multifunctional perfluoroelastomers are not commercially available and our limited laboratory samples of carboxyl polyperfluorobutadienes did not enable guidelines to be established for the elastomer formulations requirements. Thus the work to prepare some fluoroelastomer samples of various molecular weights and functionalities was initiated to provide materials for some adhesive formulation studies.

The required level of functionalities (such as the carboxyl and epoxide contents, the molecular weight of the fluoroelastomer, formulations, curing conditions versus adhesion requirements, and the fuel cell environmental compatibility) are areas that warrant future detailed investigation, because epoxy-fluoroelastomer adhesives should have qualities of hydrophobicity, oxidative stability and curing without releasing byproducts.

Preparation of Carboxyl Fluoroelastomer Adhesive Precursor--Table 2

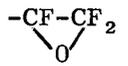
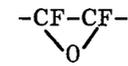
summarizes some conditions for preparation of acyl fluoride- and epoxide-containing polyperfluorobutadiene as fluoroelastomer adhesive precursors. Run 195-16 has the strongest 5.3- μ absorption peak indicating high acyl fluoride content⁴ and the presence of pendant and internal epoxide groups at 6.5 μ and 6.7 μ ⁵ respectively. The products of Runs 195-4 and 195-13 obtained by milder OF₂ treatment showed infrared with lower acyl fluoride content and also indicated terminal epoxide only. The increase in molecular weight with mild OF₂ treatment was reported.⁶ The substantial reduction of absorption peaks at 5.6 μ as compared with the starting polymer indicates that on milder OF₂ treatment reactions occur predominantly with the pendant perfluorovinyl bonds (-CF=CF₂) rather than with the internal perfluorovinylene bonds (-CF=CF-).⁷ As the concentration of OF₂ and the reaction temperature increase, the internal perfluorovinylene bonds also react and form internal epoxide as shown by the increase in the 6.7 μ infrared band. A comparison of the molecular weight and number of repeating units in Table 2, Runs 195-21 and 195-16, showed that increased polymer degradation and acyl fluoride production resulted with increased reaction temperature. Volatile degradation products were also detected with less amount for Runs 195-21 than 195-16.

Hydrolysis Procedure to Form Carboxyl Fluoroelastomer Adhesive--

Distilled water was added to a Freon 113-suspension of acyl fluoride and epoxide- containing polyperfluorobutadiene. The heterogeneous mixture was stirred at ambient temperature for 10 to 14 days. During that period the water fraction was replaced 3 to 4 times by fresh distilled water. The Freon fraction was evacuated under reduced pressure at room temperature. The residue is the carboxyl fluoroelastomer adhesive, which was dried in a vacuum dessicator at 60° overnight.

Table 2

PREPARATIONS AND PROPERTIES OF FLUOROELASTOMER ADHESIVE PRECURSORS

Run	Reaction of OF ₂ and PPFB Suspension ^a			Product							
	Static or Flow	Time (hr)	Temp (°C)	Relative Absorbance of ir Peaks					[η] ^b dl/g	Mol ^c wt	DP ^d
				 5.3 μ	-CF=CF ₂ 5.6 μ	-CF=CF- 5.8 μ	 6.5 μ	 6.7 μ			
195-4	Flow ^e	2.5	25	Weak	Medium	Medium	Weak	None	0.0399	10,700	66
195-13	Flow ^e	3.5	0								
	Static ^f	17.0	0								
	Flow ^e	3.5	0	Weak	Medium	Medium	Weak	None	0.0480	13,000	80
195-21	Static ^g	24	25	Medium	Medium	V.Weak	Medium	Strong	0.0288	6,800	42
195-16	Static ^g	24	40	Strong	Medium	None	Medium	Medium	0.0179	3,500	22

^aFreon 113-stirred suspension of polyperfluorobutadiene (Batch 10225-1B, mol wt 8500, ir peaks 5.6 μ strong and 5.8 μ medium).

^bIn octafluorotoluene at 90.0°C plus a factor of 0.0095 dl/g to convert to hexafluorobenzene at 30.1°C (Reference 6).

^cReference 6.

^dApproximate number of repeating units.

^eOF₂ bubbling under 1 atm He.

^fUnder 1 atm He and less than 0.5 atm OF₂.

^gUnder 2.5 atm OF₂ (neat).

Preliminary Formulation and Evaluation--Table 3 summarizes the preliminary results on prepared fluoroelastomer adhesives of various molecular weights and functionalities. The 10,000 molecular weight polyperfluorobutadienes with low carboxyl content give tacky and good adhesion, while high carboxyl content tends to impart brittleness.

Table 3
RESULTS ON ELASTOMERIC FORMULATION WITH
DOW DEN 438 AT 1:1 RATIO BY WEIGHT

Sample No.		Property		Comment
Acyl Fluoride PPFB ^a	Carboxyl PPFB	Acyl or Carboxyl Content	Mol wt	
195-4	194-6 ^b	Low	10,700	Brittle Tacky and very adherent
195-13		Low	13,000	Sl. tacky and very adherent
195-16	195-17 ^c	High	3,500	Brittle and adherent Sl. brittle and adherent
195-21		Medium	6,800	Brittle

^a See Table 2.

^b Hydrolyzed Sample 195-4.

^c Hydrolyzed Sample 195-16.

Scavenger Exploration

Feasibility studies of the scavenger material were initiated to reduce the loss of initial fuel cell performance due to AF-42 adhesive contamination.

To test the efficiency of the selected scavenger material in removing the leached-out basic contaminants, experiments were carried out to determine the basicity of the aqueous extract of AF-42. However, our data indicated that the aqueous extractions of uncured and cured AF-42 resins were both on the acidic side. The highest pH obtained at times between 2 and 64 hours was 6.4.

Unfortunately, our selection of the unsaturated fluorocarbon as the scavenger to consume basic amine contaminants does not apply for acidic constituents so that this approach was abandoned.

The infrared spectrum of the AF-42 adhesive sheet showed double absorption peaks at 4.58 and 4.66 μ , identified as nitrile groupings.⁸ From some of the aqueous extracts of the sample, crystalline needles were recovered and their infrared spectrum was similar to that of the AF-42 resin sample received except that they lacked the 10.3- μ absorption band and added an 11.3- μ peak.

Membrane Characterization

Infrared Analysis--All the fluorocarbon ion-exchange and the unsaponified fuel cell membranes were too thick for infrared transmission spectroscopy. The sampling procedure used for the saponified membrane was to section it by means of microtome to a 7- μ thickness, in order to avoid special handling. Another convenient method was by melting it between salt plates, but this was only applicable to the unsaponified membrane because heating charred the saponified membrane.

The ATR (attenuated total reflectance) infrared method is not recommended due to the ease of surface contamination of these membranes to distort the spectra.

The characteristic infrared absorptions for the saponified and unsaponified membranes besides the strong broad band between the 7.5- to 9.2- μ region for fluorocarbon are absorbances at 2.89 to 3.5 μ and 5.8 to 6.5 μ for the saponified membrane identified as perfluoroalkyl sulfonic acid hydrate⁹ and absorbance at 6.66 to 6.79- μ region for the unsaponified membrane identified as the sulfonyl fluoride groups.¹⁰

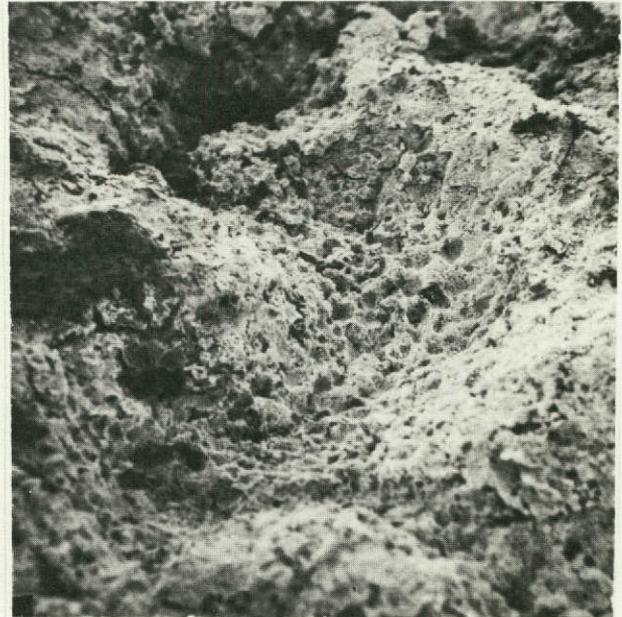
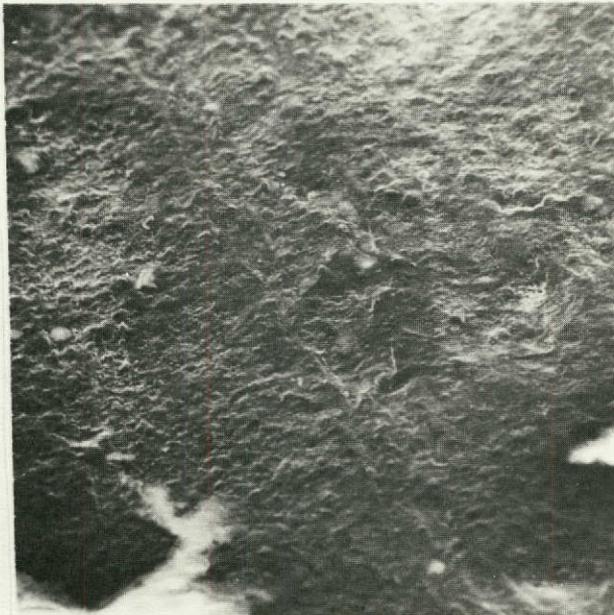
Scanning Electron Microscopic Investigation--The following series of fuel cell membrane samples was examined under the Cambridge scanning electron microscope (SEM):

- Fuel cell ion-exchange membrane as received from duPont
- Surface-platinized membrane
- Used platinized membrane with blisters after stripping in aqua regia from B/U No. 4
- New membrane with platinum dispersed throughout
- Used platinized membrane from B/U 101B Cell No. 2 after 6500 hours.

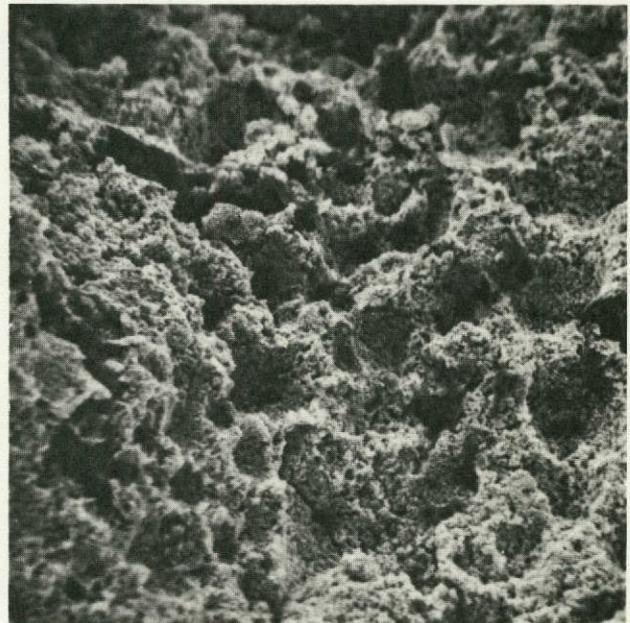
Only the first sample was vacuum-deposited with a very thin transparent layer of gold-palladium. The others were examined as received because they already were platinized. Two pieces (about 1 X 1/2 cm) of the same membrane representing both sides were mounted side-by-side for each sample observation.

Under SEM observation both sides of the ion-exchange membrane as received from duPont were smooth and looked alike, while the surface-platinized membrane was slightly rougher on one side.

For Figures 1 to 4, the beam energy of the SEM is 5 kV, the angle 45, and the mode secondary. Figure 1 shows that the two sides of the used platinized membrane with blisters after stripping in aqua regia from B/U No. 4 are very different. Since the two sides of the sample received from General Electric were not labeled as cathode or anode, smooth and rough sides are thus designated in Figure 1. The comparison of Figures 2 and 3 between the new and used membranes from B/U 101B Cell No. 2 after 6500 hours shows that a crack occurred alongside the electrode imprint on the cathode side of the used membrane only. The similar cracks along the electrode imprints are common throughout the cathode side of the used membrane showing the various degrees of cracking at different locations (Figure 4). Since the catalyst layer is thinner on the cathode side, rounding off the sharp edges of the electrode on that side may lengthen the stability of the membrane. The sharp edges may have no initial effect to cause abrasion of the catalyst surface, but after a long period (6500 hours) under fuel cell condition, the brittleness of the catalyst binder and membrane will be increased and the pliancy will be decreased. At higher magnifications of Figure 3, both cathode and anode sides show fibrous threads pulling apart at the cracks, while such structures are not observed in the new membrane on either side (Figure 2). The difference in morphology indicates possible areas of concerns. Further investigation of the implications, reasons, effect on performance and correction measures is beyond the scope of the present project.



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SMOOTH SIDE

ROUGH SIDE

FIGURE 1 SCANNING ELECTRON MICROGRAPHS OF USED PLATINIZED FUEL CELL MEMBRANE WITH BLISTERS FROM B/U NO. 4 AFTER STRIPPING IN AQUA REGIA AT MAGNIFICATIONS 500X (TOP TWO) AND 2000X (BOTTOM TWO)



CATHODE SIDE

ANODE SIDE

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FIGURE 2 SCANNING ELECTRON MICROGRAPHS OF NEW MEMBRANE WITH PT DISPERSED AT MAGNIFICATIONS 100X (TOP TWO) AND 500X (BOTTOM TWO)

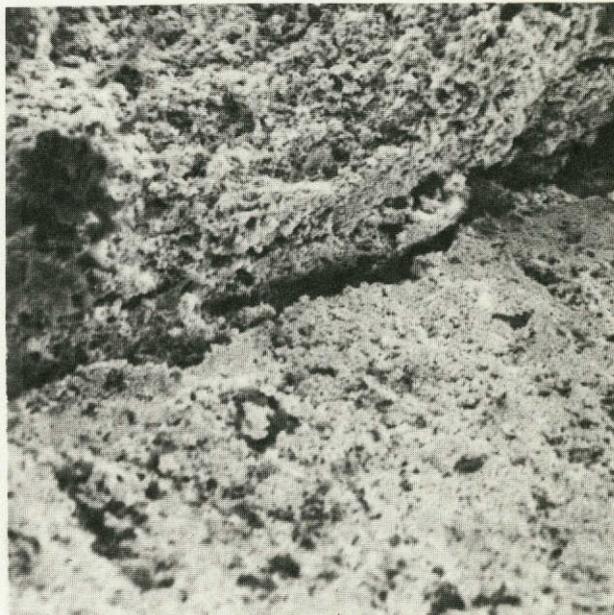
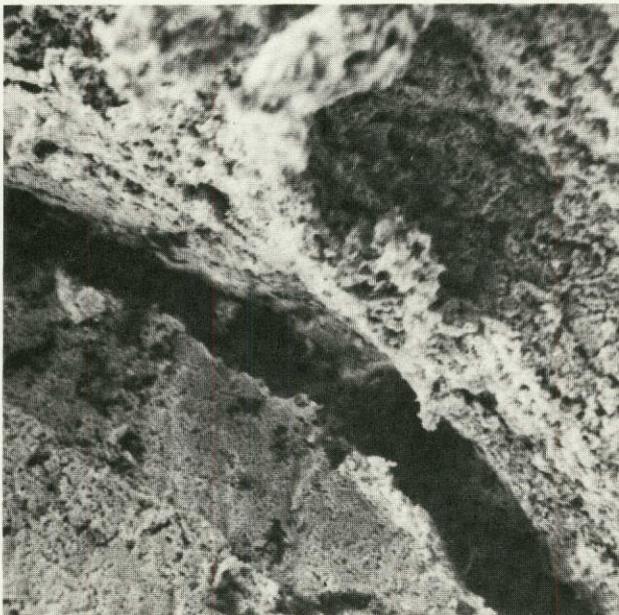
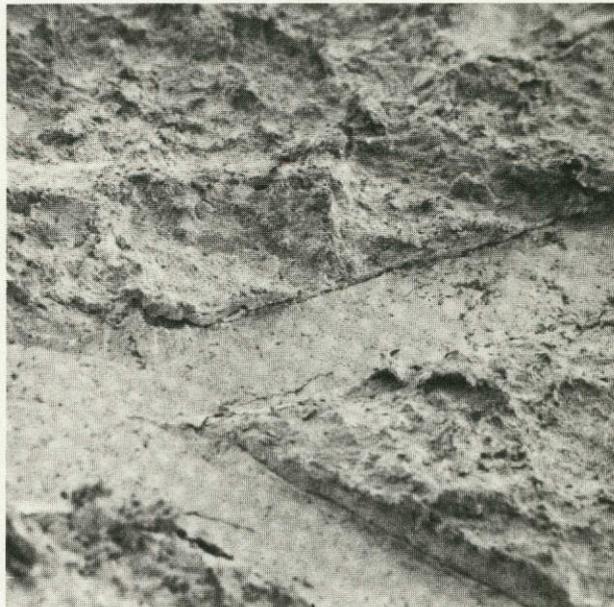
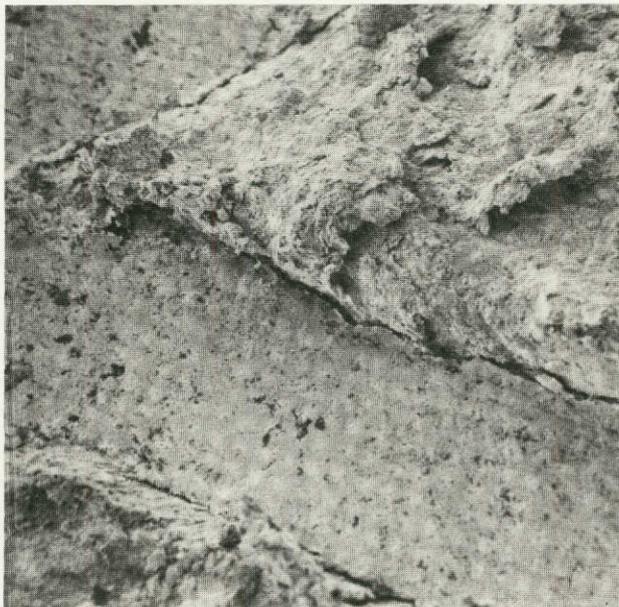


CATHODE SIDE

ANODE SIDE

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FIGURE 3 SCANNING ELECTRON MICROGRAPHS OF USED PLATINIZED MEMBRANE FROM B/U 101B CELL NO. 2 AT MAGNIFICATIONS 100X (TOP TWO) AND 500X (BOTTOM TWO)



SA-1771-22

FIGURE 4 SCANNING ELECTRON MICROGRAPHS OF USED PLATINIZED MEMBRANE FROM B/U 101B CELL NO. 2. Cathode side at different locations and at magnifications 200X (top left), 100X (top right) and 2000X (bottom two).

III CONCLUSIONS AND RECOMMENDATIONS

Membrane Adhesives

One corrective measure for the AF-42 adhesive problem would be the elimination of the contaminants. These lower molecular weight contaminants which can be extracted under aqueous conditions are leached out during cell operation and degrade cell performance. The fragments could be eliminated by improving the curing process and/or changing the formulation.

The long range stability of current adhesive resins might be improved if a sufficient quantity of fluorine was substituted for hydrogen in the component molecules.¹¹ The usual polymer degradation mechanism via oxidative instability is blocked by fluorine. Also heavily fluorinated adhesives are effective in imparting hydrophobicity in the polymer.^{12,13}

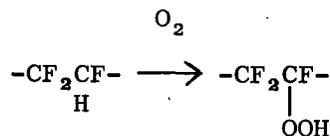
The fluoroelastomer-epoxy adhesives studied for this project are based upon the inherent nature of fluorocarbon structures to provide oxidative stability, hydrophobicity, and curing without releasing by-products. Although present epoxy-nylon type bond linkages in adhesives may have better wet environment aging properties than epoxy ester type, the suggested adhesive has advantage as being cured at much lower temperature (122°F or 50°C) than the epoxy-nylon type, which requires high curing temperature (340 ± 10°F) at the border line of overheating the polysulfone frames. Also, the general properties of carboxyl elastomers to function effectively as adhesive materials without additive¹⁴ is another advantage which could eliminate contamination problems such as found with AF-42. Thus several samples of perfluoroelastomers containing multifunctional epoxies and acids were prepared and the results are summarized in Table 1.

Membrane Stabilization

Firstly, scanning electron micrographs suggest that rounding the sharp electrode edges on the cathode side may reduce the observed cracks alongside the electrode imprint. The two reasons are: (1) these cracks are not observed for the same used membrane on the anode side nor for the new membrane on both sides, (2) the cathode side has thinner catalyst layer.

Secondly, for long range stability, the use of crosslinked perfluorinated fluorocarbon sulfonic acid membrane might reduce the physical stresses of the membrane during the wet and dry cycling under fuel cell operation. Conversely, the possibility exists of course that the properties of the present high molecular weight membrane would not be improved by crosslinking. However, a crosslinked material has not been available or tested for fuel cell applications to our knowledge so that this remains an open question for possible investigation.

Thirdly, a factor affecting membrane stabilization is the fluorination process for the unsaponified membrane. During the elimination of unstable linkages, such as $-\text{CF}=\text{CF}-$, $-\overset{\text{O}}{\text{C}}\text{F}-$ and $-\text{CFH}-$ by means of elemental fluorine treatment and decarboxylation, free radicals may be developed in the fluorocarbon chains as $-\text{CF}_2-\overset{\cdot}{\text{C}}\text{F}-$ and upon exposure to air readily absorb oxygen to give membrane degradation sites. Under the H_2/O_2 fuel cell environment the hydroperoxide-forming reaction occurs in the presence of any $-\text{CFH}-$ bond in the membrane to start membrane degradation predicted as:



similar to aging of natural rubber due to air oxidation.^{16,17}

An effective method for detection and removal of very small amounts of hydrogen atoms in the fluorocarbon backbone is needed.

The other areas of concern are uniformity of the extruded and saponified membranes, the effective thickness of the platinum catalyst layers, and the stability of the binder material in the catalyst layer. Under scanning electron micrographs, the used membrane from B/U 101B Cell No. 2 after 6500 hours showed fibrous threads pulling apart at the cracks on both cathode and anode membrane sides. Fibrous threads and delamination were not observed in the new platinized membrane. The removal of the electrode grids occurred readily for these membranes before scanning electron microscopic examinations.

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